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Dynamic Dilution System for Auditing Ambient Sulfur Dioxide Analyzers

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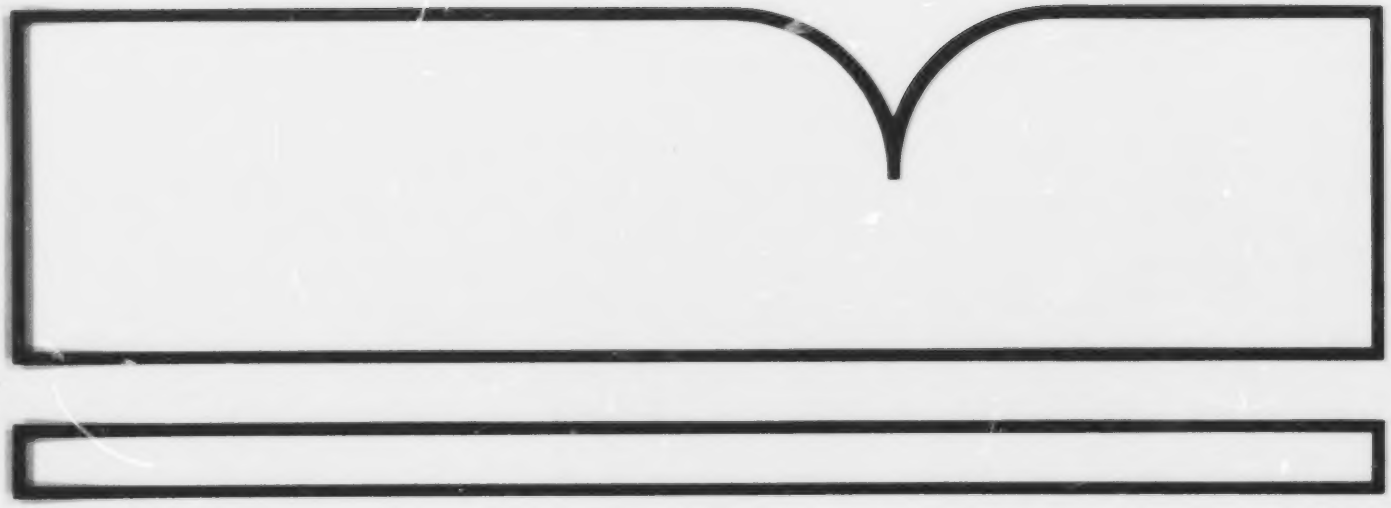

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DYNAMIC DILUTION SYSTEM FOR AUDITING AMBIENT SULFUR DIOXIDE ANALYZERS

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16. ABSTRACT

The U.S. Environmental Protection Agency has the responsibility to assess the accuracy of the air monitoring data submitted to it by the state and local agencies throughout the United States. This task is accomplished through audits administered by the National Performance Audit Program. This paper discusses a device utilized by this program to provide accurate sulfur dioxide concentrations suitable for auditing the accuracy of continuous, ambient SO_2 analyzers. Designed to be mailed to the audited agency, this compact, lightweight device has proven to be a reliable and accurate SO_2 audit system.

The development, evaluation, acceptance tests, and five years of field audit data are presented.

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DYNAMIC DILUTION SYSTEM FOR AUDITING AMBIENT SULFUR DIOXIDE ANALYZERS

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SUMMARY

A device was needed by the U.S. Environmental Protection Agency (EPA) to assess the accuracy of continuous, ambient SO_2 analyzers operated by state and local air monitoring agencies. The originally conceived device had to be rugged enough to be mailed, along with its associated compressed gas cylinders, to agencies throughout the U.S. Prototype development began in 1974 after a set of functional goals initially describing the accuracy, ruggedness and operation of the device had been developed. After two prototypes and two design changes, these goals became more realizable. In 1980 a suitable dynamic dilution device was finally accepted.

Acceptance testing provided EPA with accuracy and precision data for the devices and an insight into flow measurements. Laminar flow elements (LFE's), calibrated by the National Bureau of Standards (NBS), were used to measure the flows of the dilution devices. The high degree of accuracy obtained through using these LFE's enabled EPA to determine if the original ± 2% precision and accuracy goals were attainable. Prototype test results, acceptance test results, and the results of over 900 audits conducted since October 1980 show that the device is an extremely reliable means by which nationwide audits can be conducted.

INTRODUCTION

To determine the accuracy of the air pollution monitoring data throughout the U.S., and to relate this data quality to a common set of standards, EPA has developed a program by which continuous monitoring analyzers are annually subjected to specific concentrations of pollutants. This "audit" program was begun in the early 1970's by EPA's Environmental Monitoring Systems Laboratory at Research Triangle Park, North Carolina (EMSL/RTP). Initially a voluntary program, it has become known as the National Performance Audit Program (NPAP), and presently all state and local air pollution monitoring agencies are required to participate in it.

As a voluntary program, EMSL/RTP provided state and local laboratories with standard audit materials developed for application to the older wet chemical methods of ambient air analysis. As use of the newer automated analyzers, which measured ambient pollution levels on a continuous basis, increased, so did the need for audit devices to produce specific concentrations of pollutant gases. Thus in 1974, initial development began on a system to produce sulfur dioxide gas concentration standards by volumetric dilution, utilizing a low concentration (50 parts per million (ppm)) cylinder of sulfur dioxide and a cylinder of "zero" air. In order to meet NPAP needs, such a system should be:

1. small, lightweight and completely self-contained;
2. simple enough for operation by inexperienced personnel;
3. capable of operation without electricity;

4. fabricated to allow access only to user oriented portions;
5. independent of ambient temperature and pressure fluctuations;
6. stable enough to maintain calibration within ± 2%;
7. ruggedly constructed to allow shipment by mail;
8. used with two small cylinders of compressed gases;

This paper describes the three phases of the device's history: 1) the initial design, development and testing, 2) the audit requirements, and 3) the audit results since October 1980.

A definitive set of performance requirements and construction specifications are extremely important. Equally important are the testing procedures that are used to evaluate the system's performance requirements. The final tests are the actual field audits. The fundamental mechanical design and glass mixing chamber construction have been thoroughly tested through 5 years of constant usage. They have met and exceeded the initial design specifications.

DISCUSSION

Development and Testing

A dilution system was constructed by the National Bureau of Standards in 1974 and delivered to EMSL/RTP for evaluation. This system, which was housed in an aluminum briefcase, utilized a set of capillary tubes to deliver fixed flows of SO_2 gas from a standard concentration cylinder into a diluent stream of SO_2 free (zero) air. EMSL/RTP's initial testing of this device indicated that it was unable to generate repeatable SO_2 concentrations. A decision was made to redesign the system and, under contract, construct five, second generation devices for further testing and evaluation.

The second generation devices (Figure 1) contained two flow paths, pollutant and diluent, converging in a mixing chamber. The diluent path (Figure 2) contained a pressure regulator with gauge and a 5 liter/minute porous plug restrictor. The pollutant path consisted of a pressure regulator with gauge, a Teflon cross containing three porous plug restrictors, and three toggle valves. The combination of toggle valves and restrictors made it possible to produce seven discrete SO_2 concentration levels.

After receipt of the second generation devices, the Quality Assurance Division (QAD) of EMSL began a series of tests designed to characterize the porous plug restrictors. Since the devices would be shipped to various cities around the U.S., a number of variables had to be included in the testing procedure. These variables included ambient temperature, barometric pressure, output concentration stability, and precision.

The normal operating range for most ambient SO_2 analyzers is 20 to 30°C. Thus, three temperature tests were conducted on separate days at 20, 25, and 30°C. All tests were conducted in an environmentally controlled chamber.

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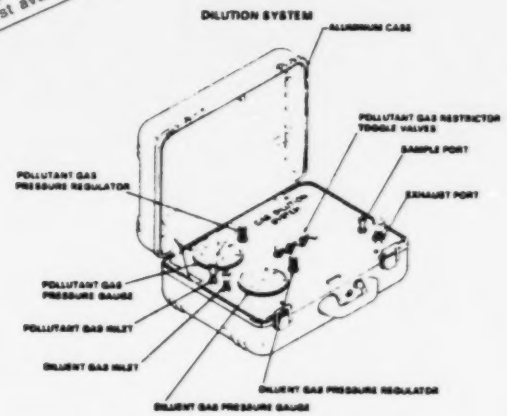

Figure 1

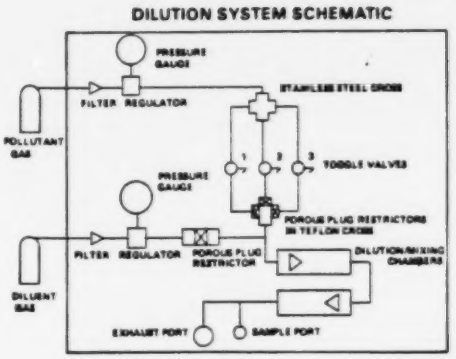

Figure 2

Since there are large differences in barometric pressures throughout the U.S., tests were conducted in two different manners. In one case flow rates for each of the pollutant flows and the diluent flow were measured daily in the laboratory for ten days. A flow ratio, pollutant flow divided by total flow, was calculated daily while comparable SO_2 output concentration levels were being obtained. This laboratory test challenged the device to only small changes in barometric pressure (750 ± 15 mm Hg). Larger variations needed to be encountered. Thus, in the second case, devices were shipped from RTP to a laboratory on the west coast. They were then taken to a high altitude (barometric pressure ≈ 630 mm Hg) site. Here the pollutant and diluent flows were measured, flow ratios were calculated, and SO_2 output concentration levels measured on a previously calibrated analyzer.

The five devices were then subjected to extensive stability and precision testing at RTP. Each device's outputs were measured on ten consecutive days at a constant temperature (25°C) with the diluent and pollutant gauges set at 30 psig. All seven output concentrations were generated and analyzed on two separate analyzers (a flame photometric detector and a pulsed fluorescence detector). The analyzers were initially calibrated against an NBS Standard Reference Material (NBS-SRM). Each analyzer was zeroed and spanned daily prior to each day's testing to ensure that the calibration curve was within ± 1% of the initial one.

The results of the prototype testing, presented in the next section, were evaluated and QAD contracted to have another twenty devices constructed. These twenty units were received in December 1979. Acceptance testing was initiated and then stopped. A change in flowmeter type revealed a construction flaw not readily apparent. Flow rates had been measured with bubble flowmeters; however, flows were now measured with LFE's. Flows through an LFE were determined by measuring the pressure drop across it, usually 15 to 220 millimeters of water. These pressures, in turn, were transmitted back into the flow system

being analyzed. Back pressures in this range produced sufficient leakage within the audit device to cause non-repeatable flow measurements. Changing the flows using the different toggle valves effectively changed the back pressure on the system and, thus, the leakage rate.

The problem was solved with a newly designed mixing chamber, and final acceptance testing was conducted from March 13, 1980 to May 7, 1980. At the beginning of the tests, an SO_2 analyzer was calibrated using a 96 ppm SO_2 standard cylinder (previously certified to an NBS-SRM cylinder). The flow for each of the toggle valves (1, 2, 3) was measured and recorded. The total pollutant flow of all valves open (1 + 2 + 3) was also measured and recorded. Using these four pollutant flow rates, four upscale SO_2 concentrations and a zero concentration were generated. Each SO_2 concentration was measured with the calibrated SO_2 analyzer and compared with the corresponding calculated output level. The calculated output (CO) was obtained by multiplying the cylinder concentration (CC) by the pollutant flow (PF) for that specific toggle valve and dividing by the sum of the diluent (DF) and the specific pollutant flow (PF).

$$CO = \frac{(CC) \times (PF)}{(DF + PF)} \qquad (1)$$

The measured output (MO) was subtracted from the calculated output (CO) and divided by the calculated output to obtain a percentage difference at each level.

$$\% \text{ Difference} = \frac{CO - MO}{CO} \times 100 \qquad (2)$$

The percentages at each level were then averaged for all 20 devices. Percentage differences were used because the output levels were not identical for all devices.

The acceptance test results and the laboratory and field evaluations of the second generation prototypes provided QAD with realistic values for the device's precision and accuracy. Accuracy and precision specifications were established based on these data, and pre- and post-audit procedures were written.

Pre-Audit Procedure

Each device had to meet the following requirements prior to an audit:

(1) each audit device had to be certified (its output concentrations remeasured) on two different days in the laboratory to establish repeatability,

(2) the percent difference between each valve combination's calculated concentration and its measured concentration had to be less than an established level,

(3) the zero air cylinders had to be analyzed to ensure that they are not contaminated with SO_2, and

(4) the audit cylinders had to be certified against an NBS-SRM.

Audit Procedure

Once the pre-audit requirements were met, the device was ready to be shipped to the audit site. Step-by-step user instructions were sent with data reporting cards to each audit participant.

The audit device, accompanied by a cylinder of SO_2 and a cylinder of zero air, was shipped to a participating state or local air monitoring agency. The agency then proceeded to use the device to audit each of their continuous SO_2 monitors. In most cases an audit would consist of a zero and 4 upscale concentrations. The highest concentration was about 80% of the analyzer's full scale response. Upon completion of each audit, agency personnel would enter the audit results on the data reporting card and mail it back to QAD. When all of the agency's SO_2 monitors had been audited, the audit device and the cylinders were returned to QAD.

Post-Audit Procedure

When returned to the lab, the audit devices underwent post-audit testing to insure that the flow ratios and output concentration regression equation were still within the prescribed specifications. If they were outside the limits, corrective steps were taken (i.e., change faulty parts, fix leaks, remeasure flows and/or reanalyze the cylinder concentration).

When the audit data were returned to QAD, a linear regression of the audited analyzer's measured concentration (Y) versus the audit concentration (X) was calculated. A copy of this regression data was then sent to the participant. If the audit device was shown to be defective by the post-audit tests and the data could not be corrected, then another audit was scheduled.

RESULTS

Development and Testing

The temperature variations between 20, 25 and 30°C had no effect on the dilution system's output. Based on the regression of analyzer response on the device's calculated output concentration, the slope throughout the 3 tests remained at 0.98 ± 0.02.

Barometric pressure tests revealed differences in flow measurements. The pollutant flows from each toggle valve were measured at barometric pressures of 745 mm Hg and at 630 mm Hg. A flow measured at 745 mm Hg was as much as 8% higher than the flow from the same toggle valve at 630 mm Hg. While each flow varied, the flow ratio, pollutant divided by pollutant plus diluent, did not. Thus, the device's output remained constant.

The stability and precision checks showed very good results. The slopes of the regression of analyzer response to audit device output concentration ranged from 0.979 to 1.014. Test results from shipping

an audit device across country showed good results as well. The calibration curve determined by the west coast lab was within ± 2% of QAD's curve. After the device was returned to QAD, the output concentrations were remeasured and again the derived calibration curve was found to be within ± 2% of its preshipment value.

The extensive acceptance testing of 20 devices provided QAD with sufficient data to establish the ± 2.0% accuracy and precision specifications for pre- and post-audit requirements. This figure is based on the slope of the regression of analyzer responses on the devices' calculated output concentrations. The output regression equation was derived using four upscale SO_2 concentrations and a zero level. Comparing the measured output levels with their corresponding calculated output levels, using equation (2), showed the relative output deviations for all 20 devices Table 1).

Table 1. Percent Difference Between Measured and Calculated Output

	Valves			
	1+2+3	1	2	3
Mean of the percent difference	-1.72	-1.78	+0.23	+1.33
Standard deviation	1.56	1.55	3.09	5.99

Each of the percent difference calculations is based on 60 data points.

In another test during this period, 216 flow measurements were taken over a span of 63 days by two different people. The total pollutant flow (valves 1 + 2 + 3) and each of the pollutant flows (valve 1, 2, 3) were measured for each device on 3 separate days. The total measured pollutant flow was subtracted from the mathematical summation of the individual flows and then divided by the total measured pollutant flow. This was done for each set of flows for each device, then averaged. The mean of the percent differences between the measured total pollutant flow and the summation of flows was -0.48% with a standard deviation of 0.236%.

Pre-Audit Results

The acceptance testing provided the data by which pre-audit requirements were established. The percent difference between each valve's calculated concentration and its measured concentration had to be less than ± 2%. Valve No. 3 provided the one exception. Its output was the lowest concentration, usually around 60 ppb, and thus its percent variability is the highest. Pre-audit experience has shown that it may vary as much as ± 5%. This variability does not, however, invalidate the primary audit requirement that the slope of the pre-audit output regression equation, derived from these four upscale concentrations and a zero, be within ± 2% of the post-audit output regression equation.

SO_2 standard gas cylinders were nominally 50 ppm. Since they were checked individually against an NBS-SRM, a specific analysis was not required from the vendor. In this case, QAD assayed and certified each cylinder's value after comparison with the NBS-SRM. Zero air cylinders contained 350 ppm CO_2, less than 0.01 ppm SO_2, and 21 percent oxygen.

Audit Results

From the first field audit in October 1980 through August 1985, these devices have been used to audit over 900 SO_2 analyzers. QAD has rated these performance audits using the following categories, where the slope and intercept are those obtained from a linear regression of audited analyzer response (Y) on the audit concentration (X):

Excellent = $0.95 \leq \text{Slope} \leq 1.05$
-3% Full Scale $\leq$ Intercept $\leq +3\%$ Full Scale

Satisfactory = $0.85 \leq \text{Slope} < 0.95$, $1.05 < \text{Slope} \leq 1.15$
-3% Full Scale $\leq$ Intercept $\leq +3\%$ Full Scale

Unsatisfactory = $\text{Slope} < 0.85$, $\text{Slope} > 1.15$
-3% Full Scale $<$ Intercept $> +3\%$ Full Scale

Table 2 was constructed using the above slope ranges. The numbers represent the percentage of audits within each criteria range.

Table 2. Quality Rating of 912 SO_2 Analyzer Audits

	Percent				
	1980/81	1982	1983	1984	1985
Excellent	40	58	58	52	62
Satisfactory	46	37	35	44	32
Unsatisfactory	14	5	7	4	6

Table 3 is a compilation by year of the means and standard deviations of the audit regression slopes and intercepts. The numbers of audits by year are also presented.

Table 3. SO_2 Audit Results

	1980/81	1982	1983	1984	1985*	Total
Number of audits	150	153	187	221	201	912
Mean of the slopes	0.9509	0.9805	0.9918	0.9918	1.0145	0.9977
Standard deviation of the slopes	0.1168	0.1025	0.1155	0.0716	0.1445	0.1153
Mean of the intercepts (ppm)	0.0009	0.0007	0.0004	0.0007	0.0014	0.0008
Standard deviation of the intercepts	0.0046	0.0035	0.005	0.0044	0.0086	0.0056

*Data through August 30, 1985

With the exception of the 1980/81 data, the audit results in Table 2 show that over 93 percent of the continuous SO_2 monitors audited yearly are within ± 15% of QAD's slope goals. The same period shows over 50% of the audits are in the "excellent" category. These are extremely good results considering the number of differing analyzers, agencies, gas manufacturers, and the myriad of other factors which may affect the

analyzers' calibrations. Table 3 shows the increasing number of participants each year. In 1983, 20 new devices were introduced into the system, accounting for the increased number of audits. Having acquired device stability experience, QAD has streamlined its pre-audit procedures.

Post-Audit Results

Another measure of the audit device's durability and ruggedness was the number of replacement items utilized in the past 5 years of service. Items replaced thus far total only 58. These include 9 pressure regulators, 7 pressure gauges, 14 flow restrictors, and 28 glass mixing chamber-manifold combinations.

CONCLUSIONS

The development history of this audit device for continuous ambient SO_2 analyzers has shown it is necessary to: 1) establish a set of performance requirements; 2) write a test protocol to evaluate the system's response to external parameters, and 3) evaluate the test equipment to determine how much it is disturbing the particular parameter under measurement. Measuring any parameter disturbs it. Thus it is necessary to determine how much the parameter is being disturbed, and will that amount of disturbance create more problems.

Abundant data documenting the accuracy and precision of the device have been presented. The accuracy of the audit device's output has been verified with analyzers calibrated with NBS-SRM's. All of the means of the percent differences for each of the output levels fully satisfy the ± 2% accuracy requirement. The device's precision is supported by the data base acquired through repeated flow measurements conducted on the 20 devices. The less than 0.5% difference between the measured total pollutant flow and the mathematical summation of the separate flows indicates precision and stability of the system.

The ruggedness and reliability of the device are found in the post-audit examination. The relatively small number of replacement items shows the device has proven its durability.

The stability of the flow ratio with changing barometric pressure, the small differences between the measured and calculated output concentrations, the low rate of equipment repair, and the overall accuracy and precision of the audits, are all factors which speak well for a device now used routinely to provide EPA with quality assurance data for the continuous sulfur dioxide monitors operating throughout the U.S.

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